# PATENT SPECIFICATION

NO DRAWINGS

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The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:— RUDOLF GAETH, RUDOLF ILGEMANN and ROLAND LINKE, citizens of the Federal Republic of Germany, residing, respectively, at 10 Weinbietstrasse, Limbergerhof/Pfalz; 18 Neuwiesenstrasse, Ludwigshafen/Rhein; and 35 Hegelstrasse, Weinheim/Bergstrasse; Federal Republic of Germany.

COMPLETE SPECIFICATION

## Production of Shaped Articles of at least One Thermoplastic Material reinforced with at least One Fibrous Material

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to the production of shaped articles of at least one thermoplastic material reinforced with at least one fibrous material.

According to the present invention there is provided a process for the production of shaped articles comprising at least one fibrous material and at least one thermoplastic material, wherein a plurality of discrete webs are provided, one web being composed of a thermoplastic material reinforced with a fibrous material and the remaining web or webs being composed of a thermoplastic material reinforced with a fibrous material, a non-reinforced thermoplastic material or a fibrous material free from thermoplastic material, the or each thermoplastic material having a torsional modulus according to DIN 53445 of at least 1000 kg/sq.cm, the webs are heated outside a shaping means to a temperature above the softening point of the or each thermoplastic material in the webs but below the softening point of the or each fibrous material therein and the webs are shaped together in superposed layers under pressure in the shaping means which has a temperature below the softening point of the or each thermoplastic material.

Preferably all the webs are composites composed of a thermoplastic material reinforced with a fibrous material. The composites may be all alike but preferably at least two of the composites differ from one another as to the thermoplastic material or the fibrous material or both. Thus, for example, a composite of polyvinyl chloride and long glass fibres may be processed with a composite of polystyrene and a textile nonwoven fabric.

Composites of fibres and certain thermoplastics may be processed into mouldings by the process according to this invention. Suitable thermoplastics are those having a torsional modulus according to DIN 53445 of at least 1000 kg.sq.cm. Thermoplastics of this type are, particularly, vinyl polymers, such as polystyrene, copolymers of styrene with other comonomers, particularly with acrylonitrile, polyvinyl chloride and vinyl chloride copolymers. Alternatively, high pressure polyethylene, low pressure polyethylene, polypropylene, copolymers of ethylene and propy-

[Price 4s. 6d.]

lene, polymethyl methacrylate, methacrylate copolymers and acrylate copolymers may be used. Polyaddition products and condensation products, such as polyamides, for example polycaprolactam, homopolymers or copolymers of other lactams or hexamethylene adipamide, and polycarbonates are also suitable for the process. It is essential that these thermoplastics have a torsional modulus (as defined above) of at least 1000 kg/sq.cm.

Fibrous substances according to this invention include fibres, woven fabrics and knitted fabrics. Endless filaments, flock, slivers, felts, mats and non-woven fabrics are also suitable. These fibrous materials may be of organic or inorganic nature. Examples of suitable materials are glass, wool, rock wool, asbestos and all types of textile fibres, for example wool, cotton and synthetic fibres. Materials having relatively long fibres, for example of 10 mm or more, are preferred. In the case of flat shapes, the elementary fibres may be shorter.

Composites are first prepared from the fibrous material and the thermoplastic material by conventional methods, such as coating, impregnation or soaking the fibres or fibrous structures with the molten thermoplastics. It may be advantageous for example to coat or impregnate a web of glass fibre matting or random-distributed slivers continuously on a support using an extruder having a sheeting die. The coated web advantageously has a thickness such that it may be wound up. The proportion of fibrous material may be 10 to 90%, preferably 15 to 50% by volume of the whole mixture. Homopolymers, copolymers or mixtures of different thermoplastics may be used for coating the fibres. It is also possible to use additives, such as pigments, flame retardants, antistatics, lubricants, slip additives, stabilisers or fillers, such as carbon black or chalk, in such amounts that adequate flow of the thermoplastic on heating is retained. The thermoplastics themselves, which are partly or wholly heated above their softening point in further processing, should contain little or no residual monomers and should have little or no crosslinking.

Since coating of flat fibrous structures may be carried out continuously at very high speeds, it is advantageous to cool the coated webs and to store them. It has been found that these composites, even when they consist of thermoplastics which are rigid at room temperature, can be rolled up. It is then possible to take from the stock any number of webs (which may be different as regards both thickness of the coating and composition), to heat them again in one operation and to shape them as described above into semi-finished goods or finished products.

For the final shaping, the webs are heated to a temperature above the softening point of the or each thermoplastic material in the webs. In some cases it is sufficient for only the surfaces of the coated webs to be raised above the softening point of the or each thermoplastic material. The webs should not, however, be heated to a temperature at which the fibrous material or materials present are softened or damaged. Heating to a temperature above the softening point of the thermoplastic material or materials may be carried out by conventional methods; for example a reinforced composite formed with fibres may be heated in a heating zone provided with infrared heating. It is also possible to use a heating tunnel or contact heating or the like. The webs which have been heated outside the shaping means to a temperature above the softening point of the or each thermoplastic material are then brought into the shaping means in which they together receive their final shape. It is essential that the shaping means is at a temperature which is below the softening point of the or each thermoplastic material. Examples of suitable shaping units are presses, rollers or pressure belts.

The particular advantage is that it is possible to use not only for example, conventional heatable moulds used for plastics materials, but also cold press moulding equipment such as is used for processing sheet metal, so that an extremely short operating cycle is possible.

It is also within the invention to use one or more webs composed of fibrous materials which are not provided with thermoplastic materials, for example non-woven fabrics, knitted fabrics, or woven fabrics, as stiffening material, or one or more webs of sheet thermoplastics material which is not reinforced, in addition to the web or webs of fibre-reinforced thermoplastics material. Metal foil layers may also be included as stiffening material. In the production of mouldings it is sometimes advantageous to prestress one or more of the composites and to allow the final moulding to cool while maintaining the tension.

The following Examples will illustrate the invention.

### Example 1

Production of a chair seat:

An open jute fabric (sacking) having a weight of 300 gm/sq.m. is coated on one side in an extruder having a sheeting die with 300 gm/sq.m. of polyethylene (density 0.960 gm/cc, $MI_2$=1.5, torsional modulus 11,000 kg/sq.cm), so that anchoring occurs at the surface. The material obtained is rolled up. ($MI_2$=melt index according to ASTM D 1238—62 T).

Using the same equipment, unbleached cotton having a weight of 150 gm/sq.m. is coated on one side with 500 gm/sq.m. of a mixture consisting of:—

100 parts of polyvinyl chloride, K value 55
4 parts of organotin stabiliser
1 part of lauryl alcohol
1 part of titanium dioxide and
0.5 part of phthalocyanine blue

and rolled up.

Sections are prepared from the coated fabric in the shape of the chair seat to be prepared.

Two plies of the jute fabric coated with polyethylene and one ply of unbleached cotton coated with PVC are passed through an electrically heated tunnel and heated to a temperature of 190°C±5°C. The sections are then piled up one upon another, the unbleached cotton forming the uppermost layer and each layer having its coated side upwards, and are placed in a press. The press is then closed at a speed of 0.5 m/sec. The temperature of the mould is kept at 40°C±10° C. The moulding pressure is 0.5 kg/sq.m. and the moulding time is three minutes.

A chair seat is obtained consisting of a homogeneous composite of the textile reinforcement and the thermoplastic materials. The chair seat is resistant to weathering and has high elasticity and stiffness.

EXAMPLE 2

Production of a corrugated sheet:

A glass cloth having a width of 1 m and a weight of 200 g/sq.m. is coated on one side on a conventional four roll calender with a mixture of:

100 parts of a copolymer of 85% of vinyl chloride and 15% of vinyl acetate with a K value of 47,

which contains:

4 parts of organotin stabiliser and
1 part of lauryl alcohol

and has a torsional modulus of 11,000 kg/sq. cm. in an amount of 200 gm/sq.m.. An identical glass cloth is coated on one side with an identical mixture in an amount of 700 gm./sq.m. The two composites may be rolled up as usual and stored.

A calendered film having a thickness of 0.15 mm is prepared from the same mixture by a conventional method.

To prepare the corrugated sheet, (a) the film, (b) the glass cloth with the 700 gm./sq.m. coating, fabric side upward and (c) the glass cloth having the 200 gm/sq.m. coating, fabric side upward are passed continuously together in the order (from top to bottom) (a), (b), (c) between infra-red lamps so that the film is heated to 160°C and the two coatings to 185°C.

At these temperatures the three plies are supplied to a continuous shaping unit consisting of a drum with an endless belt three-quarters of the way round (i.e. in principle a unit such as is conventionally used for vulcanising endless rubber bands) both the drum and the belt being provided with interengaging sinusoidal steel sections parallel to the axis of rotation. Two sections have a total height of 30 mm and the distance from crest to crest is 100 mm. They are kept at 60°C by suitable cooling means. The endless belt is forced onto the cylinder in a conventional manner by hydraulic pressure of 600 atmospheres acting on a deflecting roller. The peripheral speed of the cylinder is regulated so that the moulding and cooling time of the composite is 100 seconds.

The resultant endless sheeting corrugated transversely is translucent, weather resistant and non-inflammable. Owing to the transverse corugations it may be rolled up with a diameter of 1.80 m. The rigidity parallel to the corrugations is so great that the material may be walked upon when used as roofing and supported at intervals of 0.8 m. The weight of such roofing is only about 1.65 kg/sq.m.

EXAMPLE 3

Production of an angle section:

Glass filament cords having a weight of 300 gm/sq.m. are coated in an extruder having a sheeting die with 200 gm./sq.m. of a copolymer of styrene and acrylonitrile so that the weftless warp filaments are fixed. It is immaterial whether the individual yarns are completely impregnated or only "stuck" in place. It is sufficient that the composite obtained can be rolled up after it has cooled, without disintegrating into individual filaments.

The copolymer of 65 parts by weight of styrene and 35 parts by weight of acrylonitrile has a K value of 55 and a torsional modulus of 13,000 kg/sq.cm. A glass cloth having a weight of 150 gm/sq.m. is then coated on one side with 100 gm/sq.m. of the same copolymer on the same equipment and then rolled up.

Ten coated cord webs and eleven coated cloth webs are passed at the same time through a tunnel in which infra-red lamps are arranged one above another, and pass between the lamps so that cloth and cord alternate with cloth webs as the uppermost and lowermost webs, and each web is heated individually to a temperature of 240°C± 10°C.

At this temperature the webs are supplied to a shaping unit consisting of two shaping chains running in the same direction. Each shaping chain consists of a number of segments which have, parallel to the direction of rotation, a multi-angled section L30×4 (according to DIN 1028) having sides 30 mm long and 4 mm thick. The segments are mounted laterally in such a way that a pressure of 3 kg/sq.cm. can be applied to them. The shaping segments are kept at 25°C. The running speed is regulated so that a moulding and cooling time of 150 seconds results.

As they are fed to the "endless press", the cord webs are held under longitudinal tension of 50 kg/sq.mm. of the individual filaments, and the cloth webs under a tension of 0.3 kg/sq.cm. of web width.

Depending on the web width of the material supplied, a number of angle sections, joined together, are obtained which can be parted outside the press by means of rotary cutters.

The angle sections thus obtained having a limb length of 30 mm are corrosionproof and have a torsional modulus of 70,000 kg/sq.cm. and a tensile strength of 2500 kg/sq.cm.

EXAMPLE 4

Production of a mudguard:

A non-woven fabric having a total weight of 400 g/sq.m. (consisting of 60% by weight of glass fibres and 40% by weight of fibres of a copolymer of styrene and acrylonitrile as described in Example 3) is first prepared. The glass fibres used are entirely free from size or other binder.

Such a non-woven fabric is coated on one side with a polymethacrylate, K value 60, torsional modulus 17,000 kg/sq.cm., containing 1.5% by weight of titanium dioxide and 0.3% by weight of Indian red, through a sheeting die at the rate of 150 gm/sq.m. Two sections are then cut from the untreated non-woven fabric and one section from the coated non-woven fabric, each section having a shape corresponding to the mudguard to be prepared.

The sections pass through a tunnel oven in which they are heated to 220°C±10°C. The three sections, the coated section being at the top, are placed simultaneously into a conventional car body press and pressed. The mould of the car body press is kept at a temperature of about 70°C. The moulding time is two minutes. After removal from the mould, a mudguard is obtained which exhibits a good finish corresponding to the polish of the die. It may be mounted without aftertreatment. The mudguard has a long life because it is corrosionproof. Its high elasticity prevents denting.

EXAMPLE 5

Production of a container:

The container consists of a tubular middle section and two ends, which are made separately. Only the production of the end pieces falls within the process of the invention.

(a) Production of the tubular middle section:

Commercial non-woven glass fabric having a weight of 500 cm/sq.m. and a width of 300 mm is coated on one side with a copolymer of styrene and acrylonitrile (as described in Example 3) with 1% by weight of cadmium yellow at a rate of 300 gm./sq.m. The coating is carried out so that maximum prepreg of the non-woven fabric is obtained.

The web obtained is wound spirally onto a sheet metal cylinder so that the turns lie flush against each other. The wall of the cylinder and the web supplied to it are heated by an infra-red lamp. The web should be kept at a temperature of about 240°C.

The cylinder wall is not heated as long as web has not been wound onto it. It is only when the first layer has been applied that the lamp is switched on and provision is made for the surface of the web already wound on to be heated to a temperature of 230°C.

The cylinder which at first forms the core for the wound article consists of a cylinder of sheet metal slit longitudinally. The two longitudinal edges are fixed together by a clamping means. When the clamping means has been loosened, the sheet metal core may easily be removed from the wound tube. The web is wound spirally in the manner described and a cooled pressure roller is applied with a pressure of about 200 kg. Successive layers are applied staggered by about half the width of the web and wound in the opposite direction. After four layers have been applied in this way, the core is removed and the closing ends with their conical edges, produced as described in part b) below, are placed over the cyliindrical section.

More of the hot web is then wound spirally on to the newly formed cylindrical body the direction of the spiral winding being across the original windings, until the cylindrical portion consists of a total of fifteen layers. The webs are wound over the ends to such an extent that the web engages somewhat over the curvature of the ends in order to make an absolutely reliable bond.

(b) Production of the ends:

Circular sections are cut from the above-mentioned non-woven glass fabric, the sections being graduated in diameter. The largest diameter corresponds to the external diameter of an end, and allowance should be made for the fact, during the pressing the non-woven glass fabric is drawn, i.e. shaped. The other layers are graduated as described and made smaller to such an extent that there is a 50 mm bevel between the cylindrical part and each of the ends. A total of fifteen such graduated circular sections are prepared and heated in a tunnel oven at 230°C.

The hot sections are superposed in sequence and moulded with a pressure of 3 kg/sq.cm. in a press of conventional design. The temperature of the mould is 40°C and the moulding time is six minutes. After removal of the press, the bevel may if necessary be ground.

EXAMPLE 6

Production of a household tray:

A printed cotton cloth is coated on one side

with a polymethyl methacrylate (as described in Example 4) and in the same way an unbleached cotton cloth is coated on one side with a standard polystyrene having a K value of 66 and a torsional modulus of 12.500 kg/sq.cm. Sections are prepared from the composite having the size of the finished article, and these are brought to a temperature of 270°C. in an electrically heated chamber. For the preparation of a tray, a ply of printed composite material is introduced into a press with two plies of the unbleached cotton composite material each ply having its coated side uppermost, so that the printed cotton forms the uppermost layer. The trays are produced at a pressure of 4 kg/sq.cm. The moulding time is not more than two minutes.

EXAMPLE 7

Production of a cover plate:

A glass fibre fleece having a weight of 450 gm/sq.m. is provided on one side with a layer of 5 mm in thickness of powdered styrene/acrylonitrile copolymer having a K value of 56 and a torsional modulus of 13,500 kg/sq.cm. The copolymer is sintered onto the glass fibre fleece by heat treatment at 190° to 220°C.

Sections are prepared from the coated web in the size of the intended finished product.

Four sections are superposed each with its coated side uppermost and brought to a temperature of 220°C in an electrically heated tunnel. Then the sections are placed in a mould which has a temperature of from 20° to 40°C and shaped into a cover plate with a pressure of about 6 kg/sq.cm. for five minutes.

WHAT WE CLAIM IS:—

1. A process for the production of a shaped article comprising at least one thermoplastic material and at least one fibrous material, wherein a plurality of discrete webs are provided, one web being composed of a thermoplastic material reinforced with a fibrous material and the remaining web or webs being composed of a thermoplastic material reinforced with a fibrous material, non-reinforced thermoplasic material or a fibrous material free from thermoplastic material, the or each thermoplastic material having a torsional modulus according to DIN 53445 of at least 1000 kg/sq.cm., the webs are heated outside a shaping means to a temperature above the softening point of the or each thermoplastic material in the webs but below the softening point of the or each fibrous material therein and the webs are shaped together in superposed layers under pressure in the shaping means which has a temperature below the softening point of the or each thermoplastic material.

2. A process as claimed in claim 1 wherein each of the webs is composed of a thermoplastic material reinforced with a fibrous material.

3. A process as claimed in claim 2 wherein two of the webs differ from one another in the thermoplastic material or the fibrous material or both.

4. A process as claimed in any of claims 1 to 3 wherein the fibrous material in at least one of the webs is made of glass.

5. A process as claimed in any of claims 1 to 4 wherein the proportion of fibrous material in the webs composed of thermoplastic material reinforced with fibrous material is 10 to 90% by volume.

6. A process as claimed in claim 5 wherein the said percentage is 15 to 50%.

7. A process as claimed in any of claims 1 to 6 wherein one or more of the webs are prestressed and the tension is maintained until the shaped article has cooled.

8. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

9. Shaped article when obtained by the process claimed in any of claims 1 to 8.

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